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Analysis of Nitrogen Incorporation in Group III-Nitride-Arsenide Materials Using a Magnetic Sector Secondary-Ion Mass Spectrometry (SIMS) Instrument

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Analysis of Nitrogen Incorporation in Group III-Nitride-Arsenide Materials Using a Magnetic Sector Secondary-Ion Mass Spectrometry (SIMS) Instrument

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ABSTRACT

Group III-nitride-arsenide materials are currently under extensive study at NREL because small amounts of nitrogen can lower the alloy's bandgap significantly [1]. The growth of high-quality, low-bandgap alloys, lattice matched to GaAs is important for increasing the efficiency of multi-junction solar cells [2]. Comparisons are made among nitrogen levels measured by SIMS, bandgaps determined by a Polaron Profiler, and lattice constants measured by x-ray diffraction (XRD. The choice of primary ion beam, matrix species, nitrogen species, and determination of mass interference contributions are all important in the optimization and precision of the SIMS measurements. Quantification is discussed in relation to ion implantation standards and their measurements.

1. Introduction

The purpose of studying Group III-nitride-arsenide materials is to add low-bandgap materials to a multi-junction solar cell and increase the overall efficiency. GaAsN and GaInAsN alloys grown to date have exhibited poor optoelectronic properties. The cause of the poor quality is unknown, though it is possible that carbon and hydrogen impurities degrade these materials. Accurate and precise measurements of nitrogen in these materials are crucial. SIMS is one of the few techniques that can accurately quantify hydrogen, carbon, and nitrogen in semiconductor materials at levels of less than 1 atomic % concentration.

2. Experimental Method

The Group III-arsenide-nitride epitaxial layers were grown by atmospheric pressure metal-organic, chemical-vapor deposition (MOCVD). The rocking-mode, XRD measurements used the (400) GaAs reflection of Cu radiation. The $\Delta\theta$ values are the difference between the Bragg angle of the GaAs substrate and that of the epilayer. The nitrogen content of $GaAs_{1-X}N_X$ was estimated from $x=2x10^{-5}\Delta\theta$ (arc sec), which assumes that the layers are coherently strained. The bandgap was determined from the wavelength dependence of the photocurrent of an aqueous-semiconductor junction formed on a BioRad Polaron Profiler [3].

The SIMS measurements were performed with a Cameca IMS-5F instrument. The samples were sputtered with 14.5 keV Cs^+ at an angle of 25° from the surface normal. A square area of 150 μm x 150 μm was raster-scanned. In the sample chamber, a cryoshield at liquid nitrogen temperature was used, and the working pressure was $2x10^{-10}$ torr. The secondary ions generated from the sample were accelerated normal to its surface and were detected at 4.5 keV. The ions Ga^- and $(N+As)^-$ were collected from a 60-μm-diameter area in the center of the raster-scanned area to minimize crater edge effects.

3. Discussion of Materials

The addition of nitrogen to GaAs is known to reduce both the bandgap and the lattice constant. Fig. 1(a) shows that the shift in the Bragg angle (reduction in lattice constant) is well correlated with the decreased bandgap. Fig. 1(b) compares the nitrogen concentration measured by XRD and by SIMS. Fig. 1 implies that the XRD data can be used as an indication of the nitrogen content of GaAsN samples. Partial relaxation of the layers may introduce an error in the estimated nitrogen.

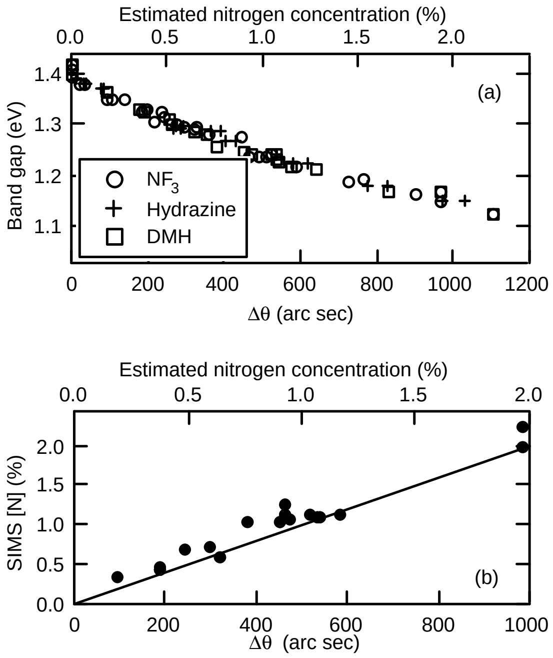

Fig. 1. (a) Bandgap and (b) nitrogen measured by SIMS plotted versus $\Delta\theta$ of the (400) reflection. Nitrogen levels are presented as a percentage of Group V, i.e., x from $GaAs_{1-X}N_X$, x =1%N = 0.5 at.%N.

In addition to N measurements, SIMS is also very useful in determining H and C contamination. Carbon levels were compared to background hole concentrations measured by capacitive-voltage profiling using a BioRad Polaron Profiler. Carbon contamination can explain much of the observed hole concentration, but not all. Efforts were made to reduce H contamination by using NF_3 as the N source and N_2 as the carrier gas with little success. Arsine is now thought to be the most likely source of the H contamination.

4. SIMS Measurement Conditions

Cs^+ is the preferred primary beam because O_2^+ sputtering induces roughening, which in turn affects depth resolution and signal levels. We also detect common light-element contaminants while sputtering with the Cs source. The matrix species Ga is preferred over As because N substitutes for As on the Group V site. At levels less than 1 atomic %, this is not an issue. At greater than 1atomic %, the margin of error increases with an increase in alloy composition. The ionization efficiency for Ga is higher while observing positive secondary ions; the reverse is true for As. For maximum precision, it is desired to detect all signals on the electron multiplier; therefore, Ga^- and As^+ are preferred.

Fig. 2 is a typical quantified depth profile of GaAsN deposited on a GaAs substrate. The nitrogen species $(N+As)^-$ was selected for higher ionization efficiency than N^+, which is subsequently higher than N^-. At levels less than 1% N, the benefits of a higher efficiency overrule the small errors introduced by N for As substitution. Hydrogen, carbon, and sometimes oxygen are introduced into GaAsN layers during growth. The SIMS instrument vacuum system also contributes to the light-element background. $(Ga+N)^-$ is avoided due to strong mass interferences from $(^{71}Ga+C)^-$ and $(^{69}Ga+O)^-$. High mass resolution can be employed; however, transmission is reduced and high precision made more difficult. High-precision sample holders are used that have been shown to improve measurement reproducibility from 24% to 4% [4].

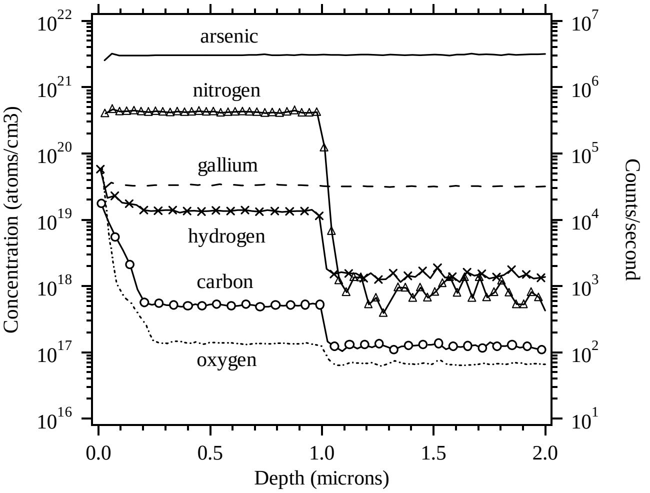

Fig. 2. SIMS depth profile of NGaAs/GaAs. Ga and As are not quantified but are plotted as raw data. Arsenic is measured on the Faraday Cup.

5. Quantification

Calibration is performed by first measuring ion implant standards to obtain relative sensitivity factors or RSFs [5]. Quantification is then obtained from C_E = (RSF) I_E / I_M [atoms/cm^3], where E is the element of interest, and I_E and I_M the secondary-ion intensity for E and the matrix, respectively. The ion implant dose is derived from the integration of the implanter current. Corrections are made for any co-implanted species identified during the implant characterization. SIMS ion implant standards are typically verified by use of the Rutherford Backscattering (RBS) technique. The detection of light elements is poor with RBS; therefore, the nitrogen standards were not verified but compared to other N implants.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were also used, but failed to detect nitrogen in these samples. The AES analysis was performed with a PHI 670 nanoprobe; the primary beam conditions were 5 kV and 20 nA. The XPS instrument used is a PHI Model 5600. The X-ray source is magnesium; accelerating voltage is 15 kV generating the Mg k-alpha X-ray. Fig. 3 shows the XPS spectrum in the region near 397 eV where N should be observed. The detection limit for nitrogen in both of these instruments is about 1 atomic %.

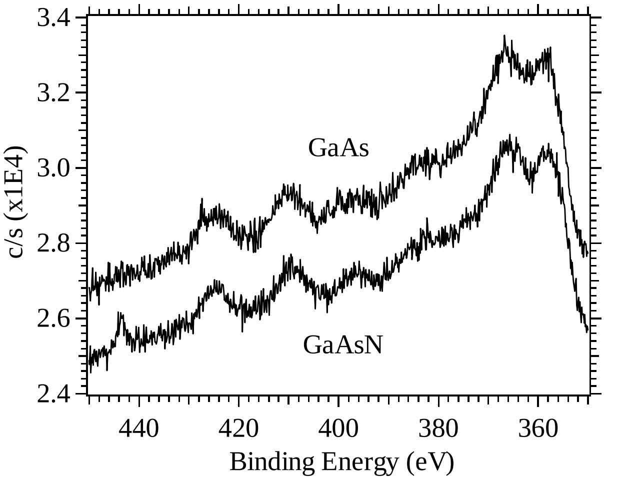

Fig. 3. XPS spectra from a GaAs wafer and a GaAsN (1 at. % nitrogen) sample. Nitrogen peak should be present at 397eV.

6. Acknowledgements

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